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FLAVOR QUALITY OF EXPLOSION PUFFED DEHYDRATED POTATO. 3. Contribution of Pyrazines and Other Compounds to the Toasted Off-flavor

SUMMARY—Potato volatile concentrates were prepared from samples of explosion puffed and conventionally dehydrated potatoes by steam distillation, extraction of distillates with diethyl ether and solvent evaporation and were analyzed by GLC. Peak heights of ten components were associated with the intensity of a toasted off-flavor produced by the puffing process. Four of these and two additional minor components were found to have pyrazine-like aromas; two components had aromas characteristic of the thermal degradation of dry proline-glucose mixtures and two components had burnt aromas. 2-Methylpyrazine, 2,5-dimethylpyrazine, furfural, 5-methylfurfural, benzaldehyde, and phenylacetaldehyde were identified by mass spectrometry and retention time. An ethylmethylpyrazine, an ethyldimethylpyrazine, and trimethylpyrazine were tentatively identified by mass spectrometry. These results suggest that the toasted off-flavor is due to the presence of alkylpyrazines, compounds derived from proline, products of sugar pyrolysis, and products of Strecker degradation reactions.

INTRODUCTION

DEHYDRATED potato dice capable of more rapid reconstitution than a conventionally dried product may be prepared by heating the semi-dry (27% moisture) precooked dice with superheated steam under pressure (1 min at 65 psi) and

suddenly releasing the pressure, resulting in an explosive expansion of the potato piece structure (Turkot et al., 1966). Explosion puffed dehydrated potatoes are sometimes subject to a characteristic flavor defect which is produced by the puffing process. Burnt and "aldehyde-like" elements of the off-flavor have been

associated with the presence of 2-methylpropanal, 2-methylbutanal, and 3-methylbutanal which can be determined by headspace vapor analysis (Sapers et al., 1970). However, an important element of the off-flavor which has been described as "toasted" cannot be attributed to these compounds (Sapers, 1970).

Roasted, nutty, popcorny and bready flavor notes in foods processed at high temperatures while in a dry state have been associated with alkylpyrazines and other heterocyclic nitrogen containing compounds (Hodge et al., 1969). A number of alkylpyrazines have been found in cocoa beans (van Praag et al., 1968), coffee (Stoffelsma et al., 1968; Stoll et al., 1967), peanuts (Mason et al., 1966) and soy products (Wilkins and Lin, 1970; Manley and Fagerson, 1970). Deck (1968) reported the isolation of eight

Table 1—Potato volatile concentrate components associated with the toasted flavor in explosion puffed dehydrated potatoes.

Peak no.	Retention Time (min) ^a	Peak height (cm)		Conventional (No toasted flavor)	Peak aroma	Identity	Method of identification ^b
		Puffed (Mod. toasted flavor)	Puffed (Sl. toasted flavor)				
18	20.9–21.6	5.10	3.10	0.40	Toasted	2-Methylpyrazine	MS, RT
19	22.1–22.2	0.70	0.65	0.25	Pyrazine	—	—
21	24.4–24.6	3.70	1.85	Trace	Pyrazine	2,5-Dimethylpyrazine	MS, RT
22	24.8–25.0	3.90	1.90	Trace	Proline degrad.	—	—
26	30.0–30.2	1.05	0.55	Trace	Pyrazine	2,3-and/or 2,5-Methyl, ethylpyrazine ^c	MS
27	31.7–31.9	Trace	Trace	Trace	Pyrazine	Trimethylpyrazine ^c	MS
29	33.8–34.4	5.10	4.25	0.70	—	Ethyldimethylpyrazine ^c	MS
					—	Furfural	MS, RT
32	39.4–40.0	0.80	0.65	0.40	Burnt	Benzaldehyde	MS, RT
33	43.2	Trace	Trace	Trace	Pyrazine	—	—
34	43.5–44.2	0.80	0.60	0.35	Burnt, Proline degrad.	5-Methylfurfural	MS, RT
35	45.2–45.7	1.60	1.10	0.40	Burnt	—	—
37	48.2–48.8	8.40	6.65	2.65	Floral	Phenylacetaldehyde	MS, RT

^aCarbowax 20M column programmed 5 min at 50°, 50–120° at 6°/min, 15 min at 120°, 120°–150° at 3°/min, 15 min at 150°.

^bMS = mass spectrometry, RT = retention time.

^cTentative.

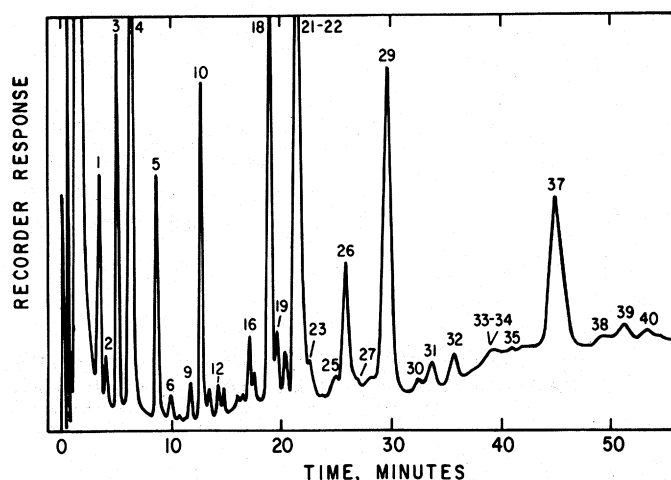


Fig. 1—Gas chromatogram of a potato volatile concentrate prepared from explosion puffed dehydrated potatoes.

alkyl-substituted pyrazines from potato chips.

Current studies have demonstrated that alkylpyrazines and other compounds associated with amino acid-reducing sugar reactions at high temperatures are present in explosion puffed dehydrated potatoes having a toasted flavor.

EXPERIMENTAL

Preparation of potato volatile concentrates

A 600g sample of dehydrated potato, ground to 20 mesh, was reconstituted with 2500 ml distilled water for 1 hr, mixed with 1000g Na_2SO_4 and 1000 ml 40% (w/v) Na_2SO_4 solution and then steam distilled at atmospheric pressure until approximately 500 ml of distillate had been collected in two equal fractions. Each distillate fraction was adjusted to pH 9 with NaOH solution, saturated with Na_2SO_4 and extracted with diethyl ether (5 × 25 ml). The ether extracts were dried with anhydrous Na_2SO_4 , pooled and evaporated under nitrogen until the volume was reduced to 1 ml. Potato volatile concentrates were prepared from samples of explosion puffed potatoes having low and moderate toasted off-flavor levels as well as from conventionally dried potatoes in which the off-flavor was absent.

Analysis of potato volatile concentrate

Potato volatile concentrates were analyzed by GLC using a 9 ft 1/8-in stainless steel column containing 20% Carbowax 20M on 60/80 acid washed Chromosorb W at a helium flow rate of 20 ml/min. The column temperature was held at 50° for 5 min, increased to 120° at 6°/min, held at 120° for 15 min, increased to 150° at 3°/min and held at 150° for 15 min.

Tentative identifications were made by comparing retention times of unknown components with those of authentic compounds using isothermal conditions appropriate to the compound being examined; additional comparisons were made of retention time and peak symmetry after potato volatile concentrates were "spiked" with authentic compounds. Identifications were confirmed by mass spectrometry using the chromatographic system described above in tandem with a CEC 103 Mass Spectrometer with a porous stainless steel GC-MS

interface. Peak 37 was trapped in a chilled capillary tube and identified by introducing it into a CEC Model 21-110B Mass Spectrometer using a direct inlet probe.

The aroma contribution of potato volatile concentrate components was established by carrying out gas chromatographic separations using the conditions and temperature program described above as well as appropriate isothermal conditions. Each analysis was performed in duplicate, once with the flame ionization detector operating to determine retention times, and once with the detector off to permit the investigators to record the aroma of the column effluent at the detector flame head as a function of time. Aromas of eluted peaks were evaluated independently (separate analyses of the same sample) by three co-workers involved in flavor research. Retention times generally were reproducible to within 0.1–0.7 min using the multi-level temperature program; however, data used to assign aromas to specific peaks showed no discrepancy between the retention time and peak width of known "marker" compounds having characteristic aromas (n-hexanal and phenylacetaldehyde) and the time during which these aromas could be detected. It was then possible to associate aromas with specific chromatographic peaks.

Volatile products of proline degradation

Proline, a normal constituent of potatoes and an important precursor of a characteristic browned flavor (Hodge et al., 1969), was evaluated as a potential contributor to the toasted off-flavor in explosion puffed potatoes. Dry equimolar mixtures of proline plus glucose were heated under nitrogen at 90–165°C for 1 to 1-1/2 hr, during which time browning and gas evolution were observed. Volatile products of the reaction were condensed out of the nitrogen stream from the reaction flask using an acetone- CO_2 (s) cold trap. The proline-glucose condensate had the typical proline degradation aroma.

A similar aroma was generated when equimolar quantities of pyrrolidine and pyruvaldehyde were mixed at room temperature; odor formation occurred rapidly and was accompanied by extensive browning. This reaction was used by Kobayashi and Fujimaki (Hodge et al., 1969) to prepare N-acetylpyrrolidine. The

mixture was vacuum distilled and the distillate retained for GLC analysis.

These preparations and a potato volatile concentrate obtained from a sample of explosion puffed dehydrated potatoes were analyzed using the Carbowax 20M column at 145°C. T_R retention time of components having aromas resembling that of heated proline-glucose were determined by the same procedure used for the examination of potato volatile concentrates.

RESULTS & DISCUSSION

STEAM distillates (adjusted to pH 9) obtained from explosion puffed dehydrated potatoes were found to have a characteristic toasted aroma similar to that of the reconstituted product. Potato volatile concentrates also possessed this aroma along with some harsh and fruity notes. Similarly prepared distillates obtained from conventionally dried potatoes had an aroma suggestive of sulfur compounds rather than a toasted aroma.

A chromatogram obtained from the analysis of 5 μl of a potato volatile concentrate prepared from explosion puffed potatoes is shown on Figure 1. The chromatographic data summarized in Table 1 was obtained from the analysis at a lower attenuation of 1 μl of volatile concentrates prepared from potato samples varying in off-flavor intensity. Peaks 21–22, seen as one large peak in Figure 1 were partially resolved on chromatograms from which these data were derived. Likewise, peak 34 was more clearly defined at the lower attenuation used for these analyses. Chromatograms for puffed and conventionally dried potato samples were qualitatively similar although some major components of the puffed samples were present only as traces in the conventional samples. This is consistent with the flavor of the products, the conventional sample being very bland. Peak heights of at least 10 components could be related to the intensity of the off-flavor. Peaks 18 and 21, major components of the concentrate, were identified by mass spectrometry and retention time as being 2-methylpyrazine and 2,5-dimethylpyrazine, respectively. Peaks 26, 27, and 29, which were smaller and/or incompletely resolved, were tentatively identified by mass spectrometry as an ethylmethylpyrazine, trimethylpyrazine, and an ethyldimethylpyrazine. In addition, unknown compounds having pyrazine-like aromas were eluted from the column in the vicinity of peaks 19 and 33; these compounds could not be seen on chromatograms or detected by mass spectrometry, presumably because of their low concentration and probable admixture with other compounds which were present at higher concentrations. A number of alkylpyrazines were found by van Praag et al. (1968) and by Bondarovich et al. (1966) to have relative retention times on Carbowax 20M consistent with the appearance of pyrazine-like aromas in the present

investigation. Alkylpyrazines may be derived from reactions between sugars and amino acids, the former being the source of pyrazine carbon atoms and the latter determining the pyrazine structure and being the source of nitrogen (Koehler et al., 1969). All of the aromas associated with pyrazines resembled but were not identical to the toasted off-flavor in explosion puffed potatoes.

Two potato volatile concentrate components eluted from the column on the downsides of peaks 22 and 34 were found to have strong aromas similar to that of a dry proline-glucose mixture subjected to thermal degradation. Compounds having similar aromas and "aroma retention times" were found to be minor components of condensates obtained from thermally degraded proline-glucose and a vacuum distillate of the pyrrolidone-pyruvaldehyde reaction mixture. It seems likely that the unknown potato components having the proline degradation aroma are derived from this amino acid and may be related to the pyrrolines and pyrroles described by Hodge et al. (1969) and by Yoshikawa et al. (1965). This aroma also bears some similarity to the toasted off-flavor in puffed potatoes.

One of the most intense odors found in the column effluent was that of phenylacetaldehyde which appeared at a time coinciding with peak 37. Retention times of phenylacetaldehyde and peak 37 were identical. This compound, furfural and benzaldehyde recently have been identified in steam volatile oils obtained from fresh potatoes (Buttery et al., 1969). Furfural and 5-methylfurfural have been identified as products of glucose (Walter and Fagerson, 1968), and sucrose (John-

son et al., 1969) pyrolysis. Phenylacetaldehyde arises from the Strecker degradation of phenylalanine (Mason et al., 1969).

It can be concluded from this research and previously reported studies (Sapers, 1970) that the toasted off-flavor of explosion puffed dehydrated potatoes represents a complex of flavor notes associated with alkylpyrazines, products of proline degradation and to a lesser extent, Strecker degradation aldehydes and products of sugar pyrolysis.

Undoubtedly, additional potato components including some which contribute to the toasted off-flavor, might be detected and identified by the selection of other procedures for sample preparation and analysis. However, a more comprehensive study of off-flavor volatiles was considered to be unnecessary in view of the primary objective of the research program, namely, to eliminate the puffing off-flavor by inhibiting those reactions responsible for the formation of the offensive compounds. Research along these lines is in progress.

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